

ATI NO. 172445
ASTIA FILE COPY

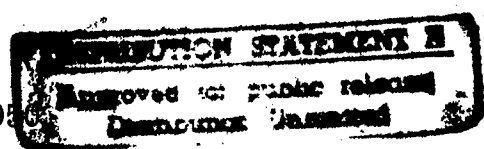
STI

UNITED STATES ATOMIC ENERGY COMMISSION

ISC-105

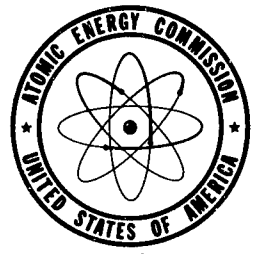
STUDY OF THE KINETICS OF THE REACTION
BETWEEN URANIUM, H_2 , HD AND D_2

By
Harry J. Svec
Frederick R. Duke



March 1, 1956

Ames Laboratory



DTIC QUALITY INSPECTED 3

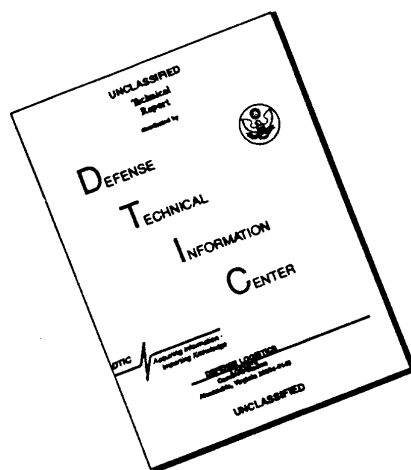
Technical Information Service, Oak Ridge, Tennessee

DTIC QUALITY INSPECTED 3

19970211 054

Incl 151

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST
QUALITY AVAILABLE. THE COPY
FURNISHED TO DTIC CONTAINED
A SIGNIFICANT NUMBER OF
PAGES WHICH DO NOT
REPRODUCE LEGIBLY.

CHEMISTRY

Reproduced direct from copy
as submitted to this office.

Work performed under
Contract No. W-7405-eng-82.

PRINTED IN USA
PRICE 15 CENTS

	Page
ABSTRACT	4
INTRODUCTION AND HISTORICAL REVIEW	4
MATERIALS	6
APPARATUS	7
Reaction tube	8
Hydrogen gas reservoir	8
Gas-flow limiter	8
Gas purification and equilibration of H ₂ , HD and D ₂ concentrations in gaseous mixtures	14
Sampling methods	14
Furnaces	15
Temperature control of furnaces	15
Manometers	16
High vacuum system	16
EXPERIMENTAL PROCEDURE	16
EXPERIMENTAL RESULTS	18
Analytical data	18
DISCUSSION	31
LITERATURE CITED	35

STUDY OF THE KINETICS OF THE REACTION
BETWEEN URANIUM, H_2 , HD AND D_2

Harry J. Svec and Frederick R. Duke

ABSTRACT

The kinetics of the reactions between uranium metal, H_2 , HD and D_2 have been examined. There is strong evidence that the reaction involves several steps of which activated adsorption of the gas by the metal is the rate governing process. Rate constants have been determined for the over-all processes in the temperature range 27.5° to 75° centigrade. Energies of activation which are of reasonable magnitude have been calculated being 10,200 calories for the process involving D_2 , 8,500 calories for the process involving HD and 8,200 calories for the process involving H_2 . From a consideration of the zero point energies for these three molecular species of hydrogen, these results follow in the right order. However because of the adsorption step and since it is not possible to determine the heat of adsorption it is impossible to state that the observed activation energies are the true activation energies. Since the heat of adsorption during the process must be considered in the final interpretation of the results, the true activation energies are probably less positive than those observed. The adsorption step in the processes also accounts for the fact that the ratios of the rates of the reactions, which may be expected to differ inversely as the square roots of the reduced masses of the gas molecules, deviate somewhat from the theoretical values.

Heterogeneous reactions such as those reported in this thesis do not lend themselves readily to kinetics experiments. Because of the reactivity of the uranium-hydrogen system it was not possible to determine to what extent the heat of adsorption enters into the values obtained for the observed activation energies. However other metal-hydrogen systems which do not interact so rapidly should better lend themselves to studies of this nature. It should then be possible to separate the adsorption-step from the reaction-step and thereby obtain the true activation energies.

INTRODUCTION AND HISTORICAL REVIEW

To test whether or not the hydrogen mass spectrometers could be applied in physical chemical research it was decided to examine the reaction between uranium metal and the three different isotopic constituents of

* This report covers Part III of a PhD thesis by Harry J. Svec.

hydrogen gas; namely H_2 , HD and D_2 . For purposes of clarity from now on only mixtures of these constituents will be referred to as hydrogen. When the opportunity arises to refer to a particular molecular species the symbols will be used. Should it be necessary to refer to the individual isotopic atoms the names protium and deuterium or the symbols H and D will be used.

It has been reported (1) that equilibrium in the reaction between uranium and hydrogen is attained very slowly. Thus under suitable reaction conditions it should be possible to determine the reaction rate of only the forward process in the reaction between metal and gas. Such an experiment may be performed if it is possible to observe the changes in concentrations of the constituents in hydrogen after the gas has been allowed to react with uranium for a short period of time. An apparatus in which the experiment could be performed may conceivably be a large thermostated vessel containing hydrogen gas a section of which contains uranium metal. Some kind of shutter interposed between the metal and gas that prevents reaction between the two would make it possible for the reaction to be allowed to proceed only at the discretion of the experimenter. Such a device presents insurmountable experimental difficulties in addition to the errors that would invariably be introduced due to insufficient opportunity of all the hydrogen molecules in the vessel to react with or even come in contact with uranium metal during the course of the experiment.

A more feasible method, one which lends itself readily to experiment, for carrying out the reactions would be to allow hydrogen to pass over uranium metal in such a way that the gas molecules have a chance to react with the metal for a short time and then are transported from the point of reaction to a place in the apparatus where no reaction can occur. Such an apparatus would consist merely of a gas reservoir connected to a tube in which the reaction takes place to which is connected another reservoir into which gas molecules, which had an opportunity to react but did not, pass. Thus if a gas molecule did not react with the metal it lacked the necessary energy required to take part in the reaction. From an observation of the rates at which the reactions took place at various temperatures the activation energy for the processes could be calculated.

To insure that each molecule of gas had a chance to react with metal the metal surface should be very large. This requirement is best met by subdividing the metal in order to get a high specific surface. Uranium metal is easily converted into a fine powder by first forming and then decomposing the hydride. By having a great excess of powdered metal available for reaction the processes would be best described as reactions of first order. Thus in the experiments described in this section of the thesis an attempt is made to keep the metal to hydrogen ratio in terms of moles on the order of 1000 to one.

A difference in the reactivities of the H_2 , HD and D_2 with uranium observed in the course of the experiments may be expected to be due essentially to the difference of their zero-point energies (2). Since the zero-point energies differ for each molecular species of hydrogen as the square root of their reduced masses the ratios of the reaction constants, k_1 for H_2 , k_2 for HD and k_3 for D_2 may be expected to vary inversely as the square roots of the reduced masses. Hence k_1/k_2 will be $2/\sqrt{3/2}$ or 1.15; k_1/k_3 will be $2/\sqrt{1}$ or 1.413 and k_2/k_3 will be $\sqrt{3/2}/\sqrt{1}$ or 1.22. Experimental difficulties may be expected to introduce slight differences in these ratios. Should the differences be great it becomes necessary to determine the extent of other effects such as adsorption upon the rate constants. There is one brief mention in the literature (1) of a study of the kinetics involved in the reaction between uranium and hydrogen. The reaction rate was observed at 3570 centigrade by following the decrease of the hydrogen pressure as the gas reacted with uranium. A rate constant was calculated for the initial rate of decrease of hydrogen pressure. A comparison of the reaction rate of D_2 with H_2 indicated the H_2 rate to be about four times that of D_2 . A description of the experiments performed by the author follow in subsequent sections of this thesis. The results obtained are indicated and discussed.

MATERIALS

Materials used in the construction of the apparatus are discussed in a later section of this thesis. The chemicals used in the experiments consisted of uranium, ordinary tank hydrogen and deuterium gas labeled 99.5 per cent deuterium.

Uranium

The metal was obtained in the form of turnings which were cut from uranium produced by the Ames group working under the Manhattan Project. While no actual analyses were available or were made upon the material its probable constitution is that given by Spedding, et. al. in their report (1) on the formula of uranium hydride. For use in subsequent experiments the turnings were cut into fine chips, washed with dilute nitric acid, rinsed with distilled water and acetone and dried under vacuum. These chips were then mixed with 10-mesh fused silica powder, which had been carefully washed with boiling concentrated hydrochloric acid, rinsed with distilled water and acetone; and introduced into the reaction tube under an atmosphere of argon which was kept in the reaction tube at all times until it was possible to evacuate the tube.

Powdered uranium was formed by first allowing the metal chips, heated to 250° C., to be completely converted to uranium hydride and then decomposing the hydride by heating to 450° C. while constantly evacuating the gas being evolved. After about two hours of such treatment, isolation of the reaction tube from the vacuum system and heating to 600° C. produced no observable pressure change in the tube. From this fact it was assumed that no undecomposed hydride remained in the reaction tube.

Hydrogen

Ordinary tank hydrogen, which had been prepared electrolytically, was used as a source of H₂ in the experiments under discussion. This material had been assayed many times using the 3-2 mass spectrometer with the HD/H₂ ratio determined to be 0.000116 ± 0.000020 which gives a D/H ratio of 1.2 parts in 20,000, a value not in variance with other reports (3, 4) on this ratio. Since the material is purified before being mixed with deuterium no other attempts were made to purify it before it was introduced into the apparatus.

Deuterium

This material as supplied by the Stuart Oxygen Company, San Francisco, California, consisted of 99.5 per cent deuterium gas. No further assay was attempted since it was used in mixtures with H₂ which were equilibrated and assayed for their H₂, HD and D₂ content.

APPARATUS

In order to study the interactions of H₂, HD and D₂ molecules with uranium metal it was necessary to have a means of (1) making up and storing mixtures of the gaseous molecules, (2) a reaction tube containing uranium and (3) a means of collecting samples of the gas mixture after it had been allowed to react with uranium. These are the essential components of the apparatus. In addition, other auxiliary components were necessary in order that the reaction between the gaseous molecules and metal could be carried out in a manner so that the data collected from the apparatus could be intelligently interpreted. A gas flow-rate limiter along with manometers for measuring pressure drops in the system were included. A purification system was added since the gases were required at the highest possible purity. The entire apparatus had to be thoroughly evacuated at various times during the experiments so a high vacuum train with its auxiliary pressure measuring devices was also included. Description of the apparatus in its entirety, which is depicted diagrammatically in Figure 1 and pictured in Figure 2, might be given better by considering the individual components in detail.

Reaction tube

The reaction tube consists of 19 millimeter outside diameter thin-walled Vycor made by sealing two Vycor-to-pyrex graded seals together. It is best to make this seal in an oxy-hydrogen flame. However, because minute bubbles invariably form at the point where Vycor is fused to Vycor, to get the seal vacuum tight it was found necessary to run a bead around the point of seal using Vycor rod about one-sixteenth of an inch in diameter. The Vycor section of the tube is about 30 centimeters long.

Because the uranium metal used in the experiments is in a finely divided state having been prepared by decomposition of the hydride, it was necessary to devise some means of keeping the powdered metal in place. Glass wool, asbestos fiber and powdered fused silica were tried for this purpose. Powdered fused silica, that would pass a 10 mesh screen but which would remain on a 20 mesh screen, proved most satisfactory for both confining the powdered metal within a limited region of the tube and allowing the hydrogen gas to pass readily through the tube. A detailed description of the filling of the tube is found in Figure 3.

Hydrogen gas reservoir

The reservoir in which pure D₂ and H₂ gases were mixed and stored consists of a two liter bulb into which was introduced a palladium filament for the purpose of equilibrating the D₂ and H₂ mixture to produce the equilibrium concentrations of H₂, HD and D₂ molecular species. It was first assumed that heating the filament to above 600° C. would cause the reaction between H₂ and D₂ molecules on the palladium metal to proceed in such a manner that the equilibrium concentrations of H₂, HD and D₂ would be quickly produced. However, final equilibrium was very slow with this device as shown in Figure 4. After four hours the value of the HD/H₂ ratio gave no indication of becoming constant. Because another means of equilibrating the gaseous mixture offered better possibilities the use of the hot palladium filament was abandoned. Conditions more favorable for establishing the equilibrium in the gas mixture may have been found using the filament but no study was made to establish them. While knowledge of these would be desirable it was felt that whatever information could be gained would apply to the particular apparatus employed in these laboratories.

Gas-flow limiter

The gas-flow limiter consists of four fine bore capillary tubes of different lengths arranged in the manner illustrated in Figure 5. This arrangement allows several possible gas flow rates if the gas is allowed to flow through each individual capillary or combinations of two or more.

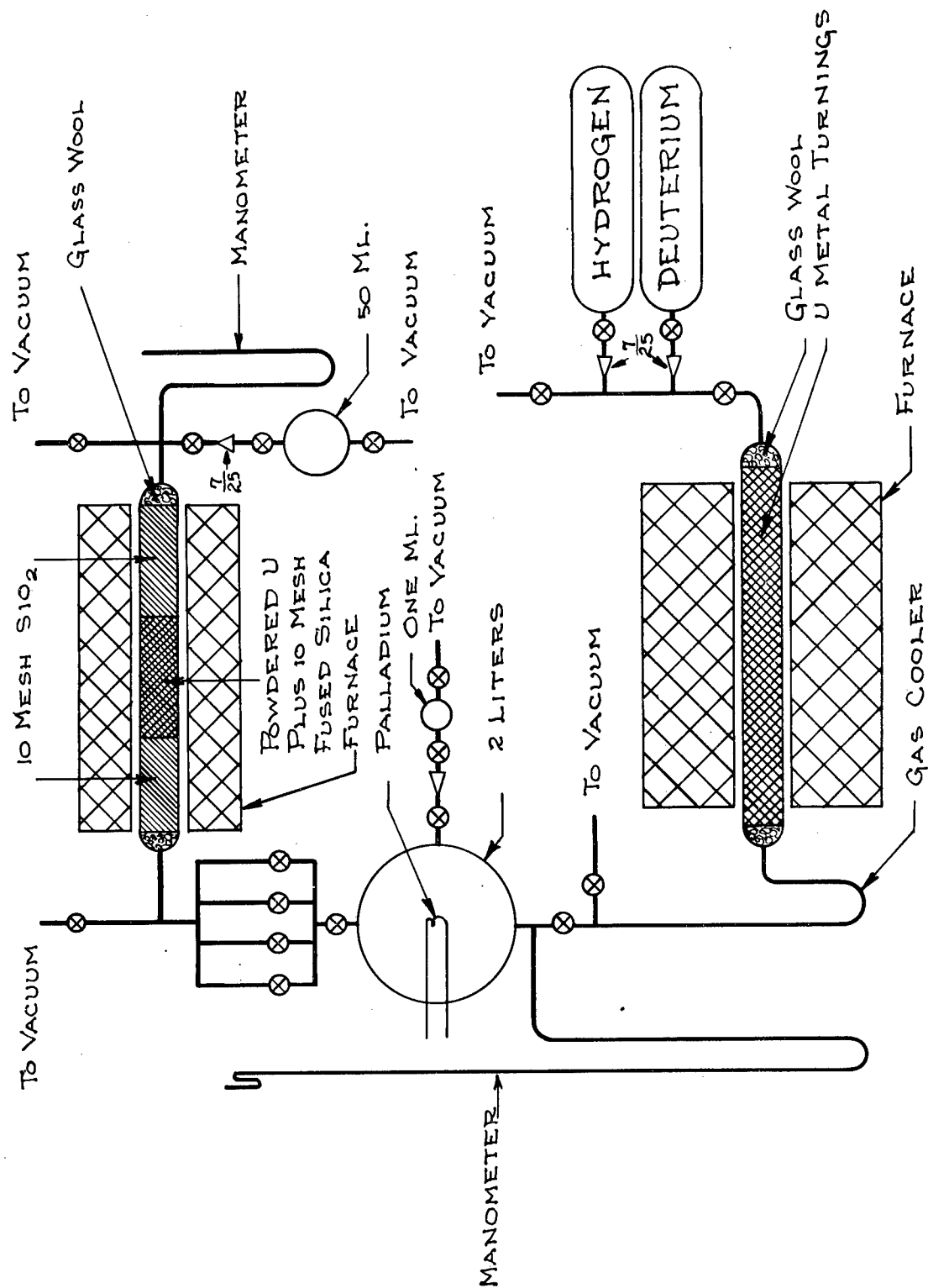


Fig. 1--Kinetics apparatus

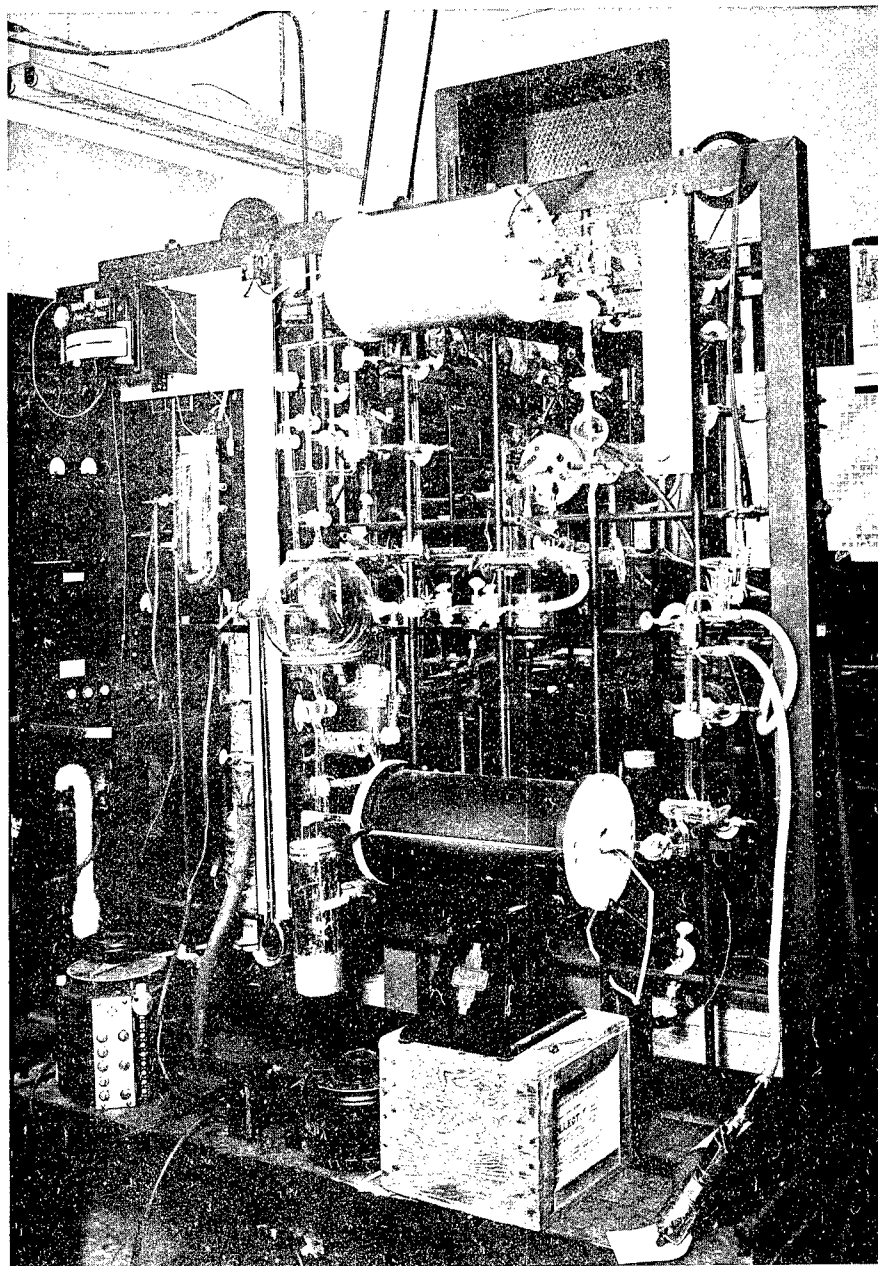


Fig. 2--Kinetics apparatus.

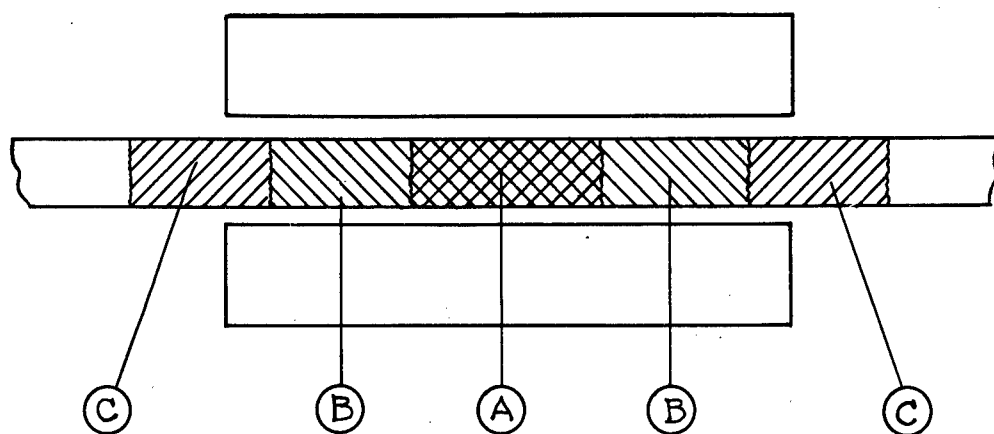


Fig. 3--Diagram of the reaction tube indicating the manner in which the filling was arranged.

- A. 30 grams Uranium, 15 grams
10 mesh fused SiO_2 , 10.5 cm.
- B. 10 mesh fused SiO_2 , 8 cm.
- C. Pyrex glass wool, 8 cm.

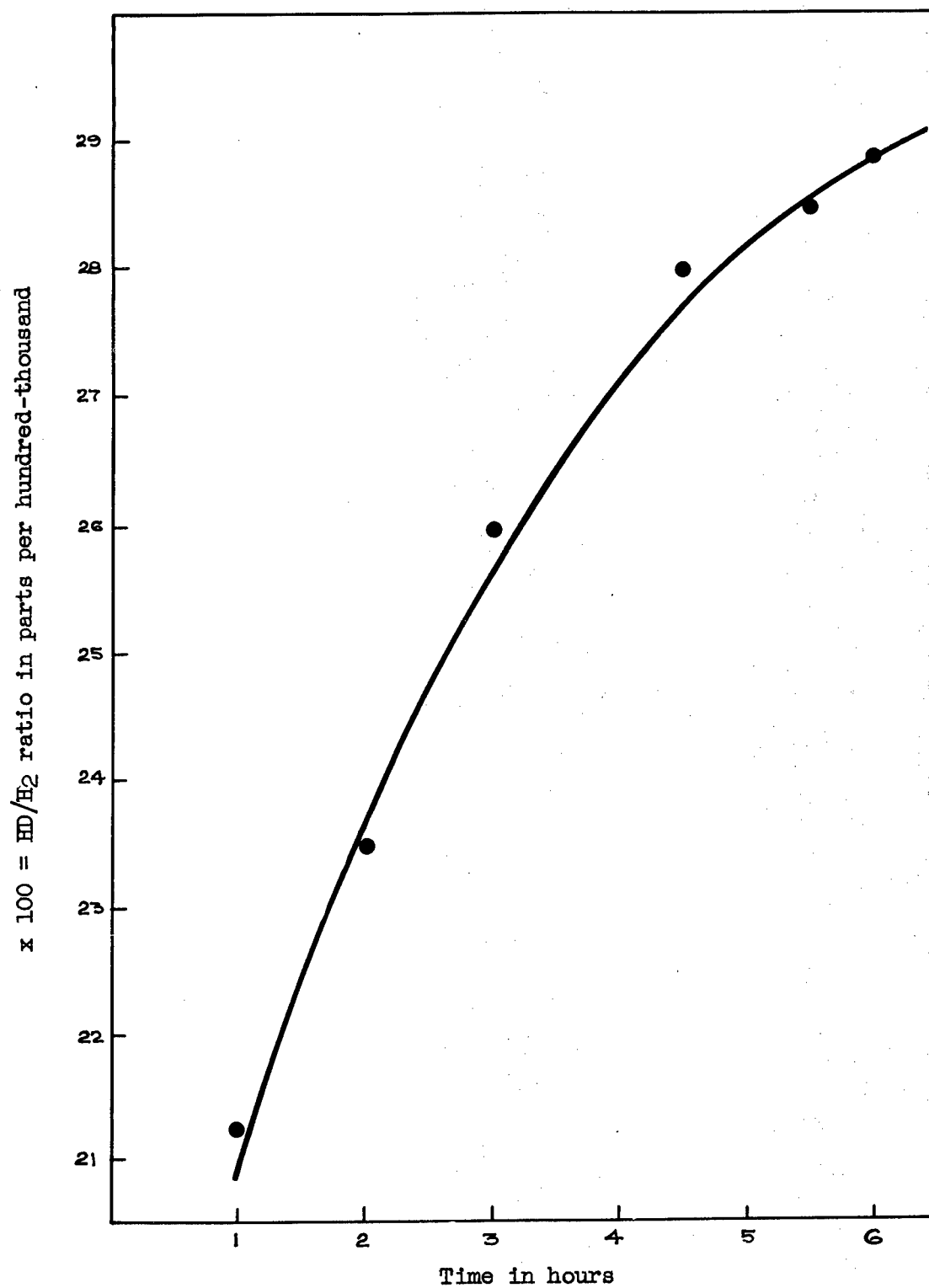


Fig. 4--Equilibration of a H₂ - D₂ mixture using a palladium filament at 650° centigrade.

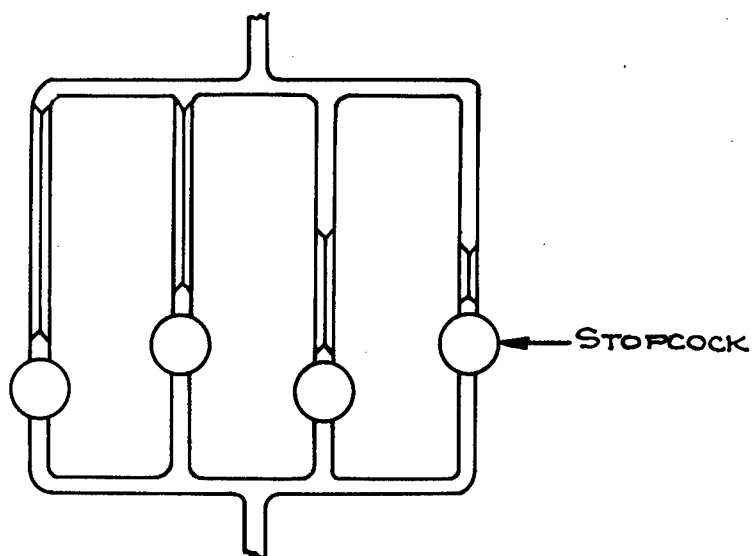


Fig. 5--Gas flow limiter

Gas purification and equilibration of H₂, HD and D₂
concentrations in gaseous mixtures

A fused silica tube, 28 millimeters in diameter and 35 centimeters long, filled with 137 grams of uranium and heated to 600° C. serves to purify the gases as they are first introduced into the two liter reservoir. Glass wool plugs in each end of the tube keep fine particles from being carried mechanically from the purification tube. The tube is connected to the rest of the apparatus by means of graded seals to pyrex glass. The uranium metal filling consists of turnings cut into pieces about 3/4 inches long.

After the reservoir is filled to about 760 millimeters pressure the temperature of the purification tube is allowed to cool to about 250-260° C. Reaction between the metal and hydrogen mixture takes place rapidly until all of the gas is consumed except that accounted for by the hydrogen in equilibrium with uranium in the above temperature range. In practice it is sufficient to allow the temperature of the purification tube to remain in this range for about one hour. Heating to 600° decomposes the hydride-deuteride formed at the lower temperature. It has been found that it is only necessary to allow the gas and metal to react once to insure equilibrium concentrations of H₂, HD and D₂. Repetition of the reaction-decomposition cycle causes no changes in these concentrations unaccountable for by experimental errors.

Sampling methods

Provision was made for collecting samples from the gas reservoir and from the gas stream which was passed over the uranium metal. A stopcock fitted with an outer 7/25 standard taper ground joint was attached to the wall of the gas reservoir; a similar device was attached to the reaction tube in a position immediately after the filling. Samples from the reservoir are collected in bulbs whose volume is about one cubic centimeter while samples from the gas stream are collected in bulbs of about 50 cubic centimeters volume. Each sample bulb was fitted with a stopcock on each side of the bulb with the inner part of a 7/25 ground glass joint connected to one of the remaining tubes leading from the stopcocks. Thus a sample bulb may be connected to either the reservoir or the reaction tube by using the mating ground glass joints. Before collecting a sample in either of the two types of sample bulbs it is necessary that all the space that may contain gases other than those of particular value in experiments, including the actual space of the bulb, be evacuated. A connection to the vacuum train manifold by means of a length of rubber tubing which serves either the reservoir or the gas stream sampling devices facilitates this operation.

Furnaces

A split-tube furnace (Hevi-Duty Electric Company, Type 70, 750 watts) was employed to heat the gas purification tube. An 18 ampere, 115 volt autotransformer (General Radio Company, Type 100 Q Variac) was used to power the furnace. With a reading of about 95 on the Variac dial the furnace temperature is about 600-650° C. A dial reading of about 25 will maintain the furnace temperature at about 250°-260° C. which is necessary for the reaction between uranium and hydrogen to proceed at the optimum rate.

The furnace used to heat the reaction tube was of special design and built locally. The thermal element consists of 19 feet of #22 chromel wire wrapped on a fused silica tube 22 millimeters inside diameter for a length of 8 inches in such a way that the temperature variation over about 7 inches of the length is constant to less than 0.5° C. at a mean furnace temperature of 475° C. The temperature at the center four inches of the furnace tube is constant to less than 0.3° C. at 475° C. Dicalite insulation surrounds the furnace tube which is contained in a galvanized tin cylinder the ends of which are made from 1/2 inch transite. Over-all length of the unit is 27 centimeters with a diameter of 7 inches. Two iron rods connected to the transite ends facilitate mounting on a rack using ordinary universal clamps. Power for the furnace is derived from two autotransformers (General Radio Corp., Type V5 Variac) the operation of which is described in the next section of this thesis.

Temperature control of furnaces

No attempt is made to control the temperature of the purification tube furnace other than setting the potential applied across the furnace terminals and letting it come to thermal equilibrium with its surroundings; the temperatures obtained in this manner lie well within ranges suitable for the experiments. Temperature indication is by means of a chromel-alumel thermocouple whose thermal junction is placed at the center of the furnace.

The reaction tube furnace temperature is controlled to $\pm 1^\circ$ C. using a Taco West Veritron indicator-controller. A chromel-alumel thermocouple serves as the thermo-sensitive element for the controller. In principle the controller is a simple on-off device; however, better temperature control is obtained by using the controller to operate a double pole double throw relay which switches one of two voltages derived from two separate autotransformers to the furnace element. One of the potentials is adjusted so that it is just low enough so that the temperature of the furnace slowly decreases while the other potential is adjusted so that the temperature of the furnace slowly increases. Thus the heating-cooling cycles of the furnace are spread out in such a manner that the furnace

temperature varies at a slow rate over a range of 2 degrees centigrade. Since any particular observations being made take place during a maximum time of about 20 seconds, it is not essential that the temperature be absolutely constant. By observing the slowly varying temperature and choosing the right moment, an experiment can be run at any predetermined reaction tube temperature with a precision conservatively estimated at $\pm 0.1^\circ \text{C.}$ at a mean temperature of 75°C.

Manometers

A full-scale mercury manometer is used to determine the pressure of the gas in the reservoir during the experiments and to serve as a means of determining the amounts of hydrogen and deuterium gss being introduced into the reservoir when making up the gaseous mixtures. The pressure changes during the time hydrogen gas is being passed over powdered uranium metal are followed by a 24 centimeter closed-end manometer located at the end of the reaction tube.

High vacuum system

A vacuum system similar to that used to evacuate the mass spectrometer tubes in these laboratories serves to evacuate the reaction kinetics apparatus. This consists of a mechanical backing pump (Welch Duo-Seal, 1400 series) in series with a two stage mercury diffusion pump (H. S. Martin Company, Type M40050 Standard). A short length of 30 millimeter pyrex tubing serves as the manifold from which any part of the apparatus may be evacuated. An ionization gage (Type 507, National Research Corporation, Cambridge, Mass.) was employed to record the pressure within the system. While it is not necessary that the very lowest possible pressures be maintained in the apparatus it is noteworthy that no trouble was experienced keeping residual pressures in the manifold below 0.01 microns (1×10^{-4} mm. of Hg). Some instances were observed when the manifold pressure was of the order of 0.002 microns.

EXPERIMENTAL PROCEDURE

It is perhaps best to discuss the experimental procedure as a series of operations in the order in which they are performed during an experiment. Mixtures of deuterium and hydrogen gases are made up by introducing into the 2-liter reservoir what are essentially H_2 and D_2 gases of known partial pressures. The gases pass, prior to being introduced into the reservoir, through a purification tube containing uranium metal heated to 600°C. To minimize contamination of the H_2 and D_2 gases due to air in the lines leading from the gas tanks to the purification tube, the

space in the lines is evacuated before opening the tank valves. A predetermined amount of each gas, as indicated by the pressure observed with the manometer, is then purified and allowed to enter the reservoir. After the mixture has been made, the gas is equilibrated by cooling the uranium metal in the purification tube to 250 to 260° C. and allowing hydride formation to take place; subsequent decomposition of the hydride by heating the purification tube to 600° C. produces a gaseous mixture whose H₂, HD and D₂ concentrations remain constant.

By opening one or a combination of stopcocks in the gas-flow limiter, a portion of the gas mixture is then allowed to pass over the powdered metal, which has been heated to a predetermined temperature. Experience has indicated that the experiments with uranium are best controlled using stopcock number 4 which at room temperature allows enough gas to pass through the reaction tube so that a 50 cubic centimeter gas sample at 100 millimeters of mercury pressure can be collected in about 15 to 20 seconds. Prior to passing the gas mixture through the reaction tube and into the sample bulb the entire space that may be involved is evacuated to less than 0.1 micron.

When enough gas has passed into the sample bulb to yield a pressure of 100 millimeters of mercury on the short manometer, the sample bulb stopcocks are closed along with the stopcock of the gas-flow limiter. Closing of the stopcocks is done as nearly simultaneously as possible. After the sample bulb is removed from the apparatus its contents are analyzed using the hydrogen mass spectrometer. For samples containing up to about 20 atoms per cent deuterium the 3-2 tube can be used by making a comparison of the intensity of the HD and D₂ ion currents as amplified by the FP-54 amplifier in addition to the normally obtained HD /H₂ ion ratio. D₂ ions are focused upon the number 3 collector plate in the 3-2 tube using an ion accelerating potential of 210 volts. From the ratios HD/H₂ and D₂/HD the D :HD:H₂ ratio can be computed.

To prepare the uranium metal so that it may be used to make further observations of the hydrogen-uranium reaction rate it is necessary to decompose any hydride which may have formed during the time of reaction. Decomposition is accomplished by heating the reaction tube to 450° C. and simultaneously evacuating the liberated gas (8). When the pressure in the vacuum system manifold drops to less than 0.1 of a micron the reaction tube is allowed to cool to room temperature or to the predetermined temperature at which the next experiment is to be performed.

EXPERIMENTAL RESULTS

Analytical data

A mixture of tank hydrogen and deuterium was made by first allowing H_2 to pass into the reservoir until the pressure was 684 millimeters of mercury and then adding D_2 gas until the pressure in the reservoir was 768 millimeters. The mixture of gas was equilibrated by forming and decomposing the uranium compound. A drop in pressure to 764 millimeters occurred due to the equilibration process. According to the make-up data the partial pressures in the mixture due to H_2 and D_2 were 684 and 84 millimeters of mercury respectively. This would correspond to a deuterium content of 10.92 atoms per cent. The average of twelve different analyses on this mixture performed on different days was 10.65 ± 0.11 atoms per cent deuterium. The discrepancy between this figure and that obtained from the make-up data which amounts to about -2.5 per cent may be accounted for by the small error introduced into the make-up figure by assuming the deuterium tank gas to be 100 per cent D_2 ; by the probable decrease in D_2 ion current during the analyses due to the "voltage effect" and by the hold-up of a proportionally greater amount of deuterium than hydrogen by the metal in the purification tube. In each of these corrections the trend is in the right direction. However, no attempt was made to apply any corrections to the ensuing analytical data since the over-all experimental errors in the experiments probably do not warrant it.

The equilibrated gas mixture was passed over the powdered metal at 27.5° , 35° , 45° , 50° , 60° , 75° and 100° C. In cases where it was possible, a 52.68 cubic centimeter sample at 100 millimeters pressure was collected. This was the case except for the 50° , 60° , 75° and 100° C. experiments in which the pressure of gas in the sample bulb rose to a maximum which was less than 100 millimeters of mercury and then decreased with varying degrees of rapidity, depending upon the temperature of the uranium metal. However, the gas samples were collected at as nearly as possible the maximum obtainable pressure for each experiment. Each sample was analyzed using the 3-2 mass spectrometer expressing the analytical results both as atoms per cent deuterium and the $D_2:HD:H_2$ ratio. Duplicate experiments were made at all reaction temperatures except 35° and 60° C. in which cases only single experiments were performed. However, these were done after data were collected from experiments run at the other temperatures. The good agreement of the single 35° and 60° C. experiments with the others indicated that duplicates were probably not necessary. Details of the experiments are summarized in Table I.

Table I

Experimental Data for Kinetics Experiments

Reaction Temp. °C.	Reservoir Temp. °C.	Atoms % D in Reservoir Gas	Δp of Gas in Res. During Experiment in mm. of Mercury	Milli- moles Hydrogen Used in Exp.	Final Pressure of Sample in mm. of Mercury*	Atoms % D in Sample	Time to Collect Sample in Secs.
27.5	27.5	10.62	8	0.908	100	10.86	15.6
35.0	27.0	10.65	9.5	1.078	100	11.17	16.3
45.0	29.0	10.70	11.5	1.297	100	11.50	17.0
50.0	27.5	10.67	12.5	1.353	88	11.62	18.7
60.0	27.0	10.65	14	1.593	80	12.21	14.7
75.0	27.0	10.60	16	1.816	62	12.90	8.8
100.0	27.0	10.65	18	--	5**	--	--

*Volume of all samples was 52.68 cubic centimeters.

**Not enough material was collected to make an analysis. Due to the reaction between the uranium and hydrogen the value 5 millimeters represents a maximum which decreased very rapidly. No further experiments were performed at temperatures higher than 100° C.

As indicated in the table it was impossible to perform any reliable experiments at 100° C. because the reaction between metal and gas proceeded so rapidly that a maximum pressure of about 5 millimeters of mercury was observed in the sample bulb. Data from the reservoir gas and sample analyses appear broken down into essential categories in Table 2.

Table II
Breakdown of Analytical Data

Gas Sample Analyzed	HD/H ₂	D ₂ /HD	Ratio D ₂ : HD: H ₂	Moles Per Cent D ₂	Moles Per Cent HD	Moles Per Cent H ₂
Reservoir	0.244	0.0457	1:21.9:89.7	0.89	19.45	79.66
27.5° C.	0.252	0.0461	1:21.7:86.2	0.92	19.92	79.15
35.0° C.	0.257	0.0523	1:19.1:74.3	1.06	20.25	78.69
45.0° C.	0.262	0.0567	1:17.7:67.4	1.16	20.56	78.28
50.0° C.	0.267	0.0573	1:17.4:65.4	1.19	20.76	78.04
60.0° C.	0.282	0.0607	1:16.5:58.5	1.32	21.72	76.96
75.0° C.	0.300	0.0676	1:14.8:49.3	1.54	22.73	75.73

From a consideration of Figure 6 which is a diagrammatic representation of the reservoir, gas-flow limiter, reaction tube and sample collecting device, further information which is necessary to evaluate the experimental data, is obtained.

The volumes of space in which gas may be held in the apparatus may be divided into AD, the region in which the gas never has had a chance to react with uranium; DE the region in which reaction occurs and EB the region in which the gas which has had an opportunity to react no longer can react with uranium. The volumes of the free space in each of these regions is A to D, 41.4 cc.; D to E, 12.2 cc.; E to C, 47.4 cc. and C to B 52.68 cc. The total volume between points A and C was determined by allowing argon gas at a known pressure to expand from the space AC into the space CB. Since the volume BC was accurately determined at 27.0° C., the volume in space AC could be calculated using the perfect gas law. The average of several such determinations, designed to produce a final pressure after expansion of about 100 millimeters of mercury in order to obviate volume corrections in the manometer, was 101.0 cubic centimeters ± 0.2 per cent. The free volumes in regions A to D, D to E, and E to C were estimated from the dimensions of the reaction tube and from liquid displacement measurements made on a replica which was nearly the same as the reaction tube as possible except for the omission of powdered uranium in the filling. The estimated volumes in these regions are probably accurate to ± 0.5 cubic centimeters.

By considering the apparatus broken down into various regions and with their respective volumes determined it is possible to separate the amount of hydrogen used in the experiments into (1) the amount that never had a chance to react with uranium, (2) the amount that had a chance to react and then passed beyond what is given as point E in Figure 6, (3)

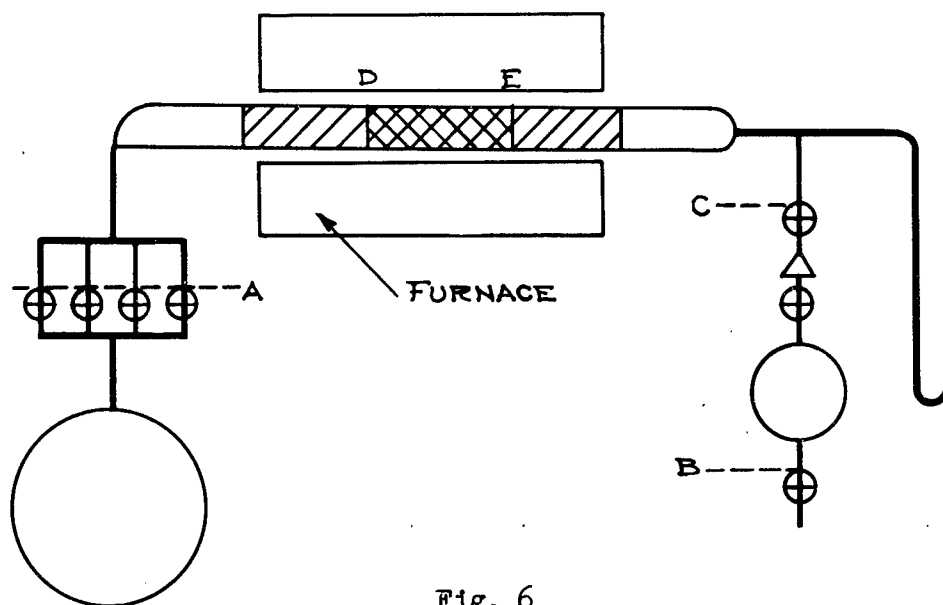


Fig. 6

the amount held in the free space of region D to E and (4) the amount which reacted with uranium to form the hydride. The sample taken for analysis represents about 53 per cent of (2) and so it is assumed that its composition represents that of all the gas which has passed the point beyond the uranium in the reaction tube. In calculations concerning the actual number of millimoles of hydrogen held in the space of each region of the apparatus account must be made of the fact that temperature differences are present within a particular region. In both regions AD and EC 5.4 cubic centimeters of the total volume are at the reaction tube temperature while in 5.7 cubic centimeters of the volume the temperature varies from that of the reaction tube to room temperature. The remainder of the volume of each region is at room temperature. Table 3 summarizes the data obtained from calculations regarding the number of millimoles hydrogen contained in each region of the apparatus at the time the sample is collected in each of the experiments.

Table III
Hydrogen Held in Various Regions of the Apparatus

Reaction Temp. in °C.	Millimoles Hydrogen Which Have Passed Point E	Millimoles Hydrogen in Interstices of DE	Millimoles Hydrogen Not Passing Point D	Millimoles Hydrogen Reacted With Uranium
27.5	0.535	0.065	0.222	0.086
35.0	0.529	0.064	0.220	0.265
45.0	0.503	0.062	0.217	0.515
50.0	0.467	0.053	0.192	0.641
60.0	0.420	0.047	0.173	0.953
75.0	0.328	0.035	0.133	1.320

It might be well to call attention to the data presented in column four of the table. While the volume of gas held in the region AD is essentially constant (volume corrections due to the expansion of the Vycor are negligible), the number of moles contained in the space of this region diminishes due to an increase in temperature of a part of the region.

From the data presented in Table III it is possible to calculate the ratios of the rate constants for the reactions between uranium, H₂, HD and D₂. In any of the experimental data observed the ratio of moles uranium available for reaction to the total moles of hydrogen used in the experiments is about 1250/1.0 to 1.8. Thus it is expected that the rate of disappearance of any molecular species of hydrogen would conform to a

first order expression. Hence it may be stated that

$$-\frac{dp_{H_2}}{dt} = k_1 p_{H_2} \quad (1)$$

$$-\frac{dp_{HD}}{dt} = k_2 p_{HD} \quad (2)$$

$$-\frac{dp_{D_2}}{dt} = k_3 p_{D_2} \quad (3)$$

From (1) and (2)

$$\ln p_{H_2} = \frac{k_1}{k_2} \ln p_{HD} \quad (4)$$

From (1) and (3)

$$\ln p_{H_2} = \frac{k_1}{k_3} \ln p_{D_2} \quad (5)$$

and from (2) and (3)

$$\ln p_{HD} = \frac{k_2}{k_3} \ln p_{D_2} \quad (6)$$

Integration of (4) leads to the expression

$$\frac{\ln p_{H_2}^0}{p_{H_2}} = \frac{k_1}{k_2} \frac{\ln p_{HD}^0}{p_{HD}} \quad (7)$$

Equations (5) and (6) lead to similar results.

To determine p^0 , the initial pressure for the reactions it is necessary to determine what the pressure would have been in the reaction tube assuming that no hydrogen reacted with uranium. Column five of Table III gives the millimoles of hydrogen which reacted at each experimental temperature. From a consideration of the perfect gas law and the volume of the apparatus from a point half way between points D and E and point B of Figure 6, this being a reasonable estimation of the space which the gas would occupy, it is possible to calculate the apparent initial pressure. However, except in the case where the reaction was run at room temperature a complication arises. Part of the volume in which the gas would be contained is at the reaction temperature while the remainder is at room temperature. From a consideration of the dimensions of the apparatus 15.3 cubic centimeters of the total volume is at the reaction temperature. The total volume of the space which extends from point B to the point half way between D and E in the apparatus is 106.2 cubic centimeters. Thus 90.9 cubic centimeters of the total volume of gas will

be at room temperature.

To determine the pressure at which the gas would be if no reaction with uranium had taken place consider first that the hydrogen that reacted with uranium occupies volume V_2 (which is 15.3 cubic centimeters) at temperature T_2 . Since n moles of hydrogen reacted it is possible to calculate the pressure this amount of gas would exert upon the walls of V_2 at T_2 . Then after allowing this gas to expand into volume V_1 (90.9 cubic centimeters) at temperature T_1 the problem is to determine the resultant pressure. Figure 7 indicates what the situation is diagrammatically.

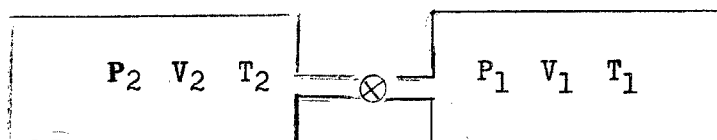


Figure 7

The gas is first held in the left vessel where

$$n = \frac{P_2 V_2}{RT_2} \quad (8)$$

Then the stopcock is opened and the pressure decreases to P_r in both left and right vessels.

$$n_2 = \frac{P_r V_2}{RT_2} = \text{number of moles of gas in the left vessel.} \quad (9)$$

and

$$n_1 = \frac{P_r V_1}{RT_1} = \text{number of moles of gas in the right vessel.} \quad (10)$$

However, since $n = n_1 + n_2$

$$n = \frac{P_r}{R} \left[\frac{V_1}{T_1} + \frac{V_2}{T_2} \right] \quad (11)$$

or

$$P_r = \frac{nRT_1T_2}{V_1T_2 + V_2T_1} \quad (12)$$

For the experiment at room temperature when $T_2 = T_1$

$$P_r = \frac{0.086 \times 10^{-3} \times 82.05 \times 300.5 \times 760}{106.2}$$

or

$$P_r = 15.15 \text{ millimeters of mercury}$$

However the actual pressure observed (see Table 1) when the sample was collected was 100 millimeters, thus p^0 for this experiment is the sum of the resultant pressure plus the sample pressure or 115.2 millimeters of mercury which represents the total initial hydrogen pressure. To find the initial partial pressures for each of the molecular species of hydrogen it is necessary to multiply this total p^0 by the mole fraction of each molecular species which is found in columns 5, 6 and 7 of Table 2 considering the values of the mole fractions for the unreacted reservoir gas.

The final total pressure p of equation (7) is that pressure at which the sample was collected. Thus to determine the final partial pressures of each molecular species of hydrogen, it is necessary to multiply the sample pressure which is found in Table I for each of the experiments by the mole fraction of each molecular species considering the values of the mole fractions for the sample obtained in the experiment under examination. Table 4 summarizes the calculated initial and final partial pressures for the experiments.

Table IV

Initial and Final Partial Pressures for
H₂, HD and D₂ in Hydrogen

Exp'l in °C.	Total p ^o	p ^o _{H₂}	p ^o _{HD}	p ^o _{D₂}	Total p	p _{H₂}	p _{HD}	p _{D₂}
27.5	115.2	91.8	22.4	1.03	100	79.2	19.9	0.92
35.0	146.7	116.8	28.6	1.31	100	78.7	20.3	1.06
45.0	192.0	153.0	37.4	1.71	100	78.3	20.6	1.16
50.0	202.0	161.0	39.3	1.80	88	68.7	18.3	1.05
60.0	250.0	199.3	48.6	2.21	80	61.6	17.4	1.06
75.0	299.0	238.0	58.2	2.66	62	46.9	14.1	0.95

All pressures indicated in this table are in millimeters of mercury.

Substitution of the proper values from Table 4 into formulae (5), (6) and (7) gives the ratios of the rate constants k_1 , k_2 and k_3 . As an example these ratios are calculated for the experiment at 27.5° C.

$$\log \frac{79.2}{91.8} = \frac{k_1}{k_2} \log \frac{19.9}{22.4}$$

$$\frac{k_1}{k_2} = \frac{-0.065}{-0.052} = 1.25$$

$$\log \frac{79.2}{91.8} = \frac{k_1}{k_3} \log \frac{0.92}{1.03}$$

$$\frac{k_1}{k_3} = \frac{-0.065}{-0.049} = 1.33$$

$$\log \frac{19.9}{22.4} = \frac{k_2}{k_3} \log \frac{0.92}{1.03}$$

$$\frac{k_2}{k_3} = \frac{-0.052}{-0.049} = 1.06$$

In a similar manner these ratios are calculated from the data of experiments at other temperatures and the results are tabulated in Table 5.

Table V
Ratios of Rate Constants for Reaction
Between Uranium, H₂, HD and D₂

Exp'l Temp. in °C.	k ₁ /k ₂	k ₁ /k ₃	k ₂ /k ₃
27.5	1.25	1.33	1.06
35.0	1.15	1.83	1.60
45.0	1.13	1.71	1.44
50.0	1.11	1.58	1.42
60.0	1.14	1.60	1.40
75.0	1.14	1.58	1.30

Using equations (1), (2) and (3), the data in Table 4, and column eight of Table I, the rate constants for each reaction over the range of temperatures used in the experiments may be calculated. Such a calculation is included here for the experiment at 27.5° C.

From (1) upon integration there results

$$-\ln p_{H_2} = k_1 t + C \quad (13)$$

where C is the constant of integration.

Integrating between initial and final conditions for the experiments

$$-\ln \frac{p_{H_2}^0}{p_{H_2}} = k_1 (t_2 - t_1) \quad (14)$$

$$\ln \frac{p_{H_2}}{p_{H_2}^0} = k_1 (t_2 - t_1) \quad (15)$$

Converting to base ten logarithms

$$\log \frac{p_{H_2}}{p_{H_2}^0} = \frac{1}{2.303} k_1 (t_2 - t_1) \quad (16)$$

Similarly, expressions may be derived from equations (2) and (3) to give

$$\log \frac{p_{HD}}{p_{HD}^0} = \frac{1}{2.303} k_2 (t_2 - t_1) \quad (17)$$

and

$$\log \frac{p_{D_2}}{p_{D_2}^0} = \frac{1}{2.303} k_3 (t_2 - t_1) \quad (18)$$

Using the data from Tables I and IV for the 27.5° C. experiment

$$\log \frac{91.8}{79.2} = \frac{15.6}{2.303} k_1$$

$$k_1 = \frac{2.303 \times 0.064}{15.6} = 0.00945 \text{ sec.}^{-1}$$

Calculated in a similar manner

$$k_2 = 0.00752 \text{ sec.}^{-1}$$

and

$$k_3 = 0.00707 \text{ sec.}^{-1}$$

Results of similar calculations for the experiments at other temperatures are listed in Table VI.

Table VI

Rate Constants for the Reaction
Between Uranium, H₂, HD and D₂

Exp'l temp. in °K.	1/T x10 ⁻²	k ₁ in sec. ⁻¹	log k ₁	k ₂ in sec. ⁻¹	log k ₂	k ₃ in sec. ⁻¹	log k ₃
300.5	3.33	0.00945	-2.025	0.00752	-2.124	0.00707	-2.152
308.0	3.25	0.0243	-1.615	0.0212	-1.674	0.0130	-1.886
318.0	3.15	0.0398	-1.401	0.0352	-1.454	0.0229	-1.641
323.0	3.10	0.0455	-1.342	0.0408	-1.389	0.0301	-1.522
333.0	3.00	0.0798	-1.098	0.0697	-1.156	0.0500	-1.301
348.0	2.79	0.1843	-0.7351	0.1605	-0.795	0.1168	-0.933

From the data of Table VI the energy of activation for the reactions may be calculated by making use of the Arrhenius relationship

$$\frac{d \ln k}{d T} = \frac{E}{RT^2} \quad (19)$$

whose integrated form is

$$\ln k = - \frac{E}{RT} \text{ const.} \quad (20)$$

in which it is seen that the relationship between $\ln k$ and $1/T$ is linear. Plotting the data listed in Table VI should result in a straight line the slope of which is $-E/R$ from which the activation energy may be calculated. Such a plot is made in Figure 8 from which it is evident that all the data except those obtained for the 27.5° Centigrade experiment have a linear relationship when the Arrhenius equation is applied.

The energies of activation of the processes are $8,200 \pm 200$ calories for that involving H₂ molecules, $8,500 \pm 200$ calories for that involving HD molecules and $10,200 \pm 200$ calories involving D₂ molecules. Following reasoning similar to that previously cited in the literature based upon a consideration of the zero point energies of D₂, HD and H₂ molecules, the energy required for activation in the uranium -D₂ reaction should be greater than that for the uranium -H₂ reaction. The magnitudes of the observed activation energies are what may reasonably be expected for such reactions.

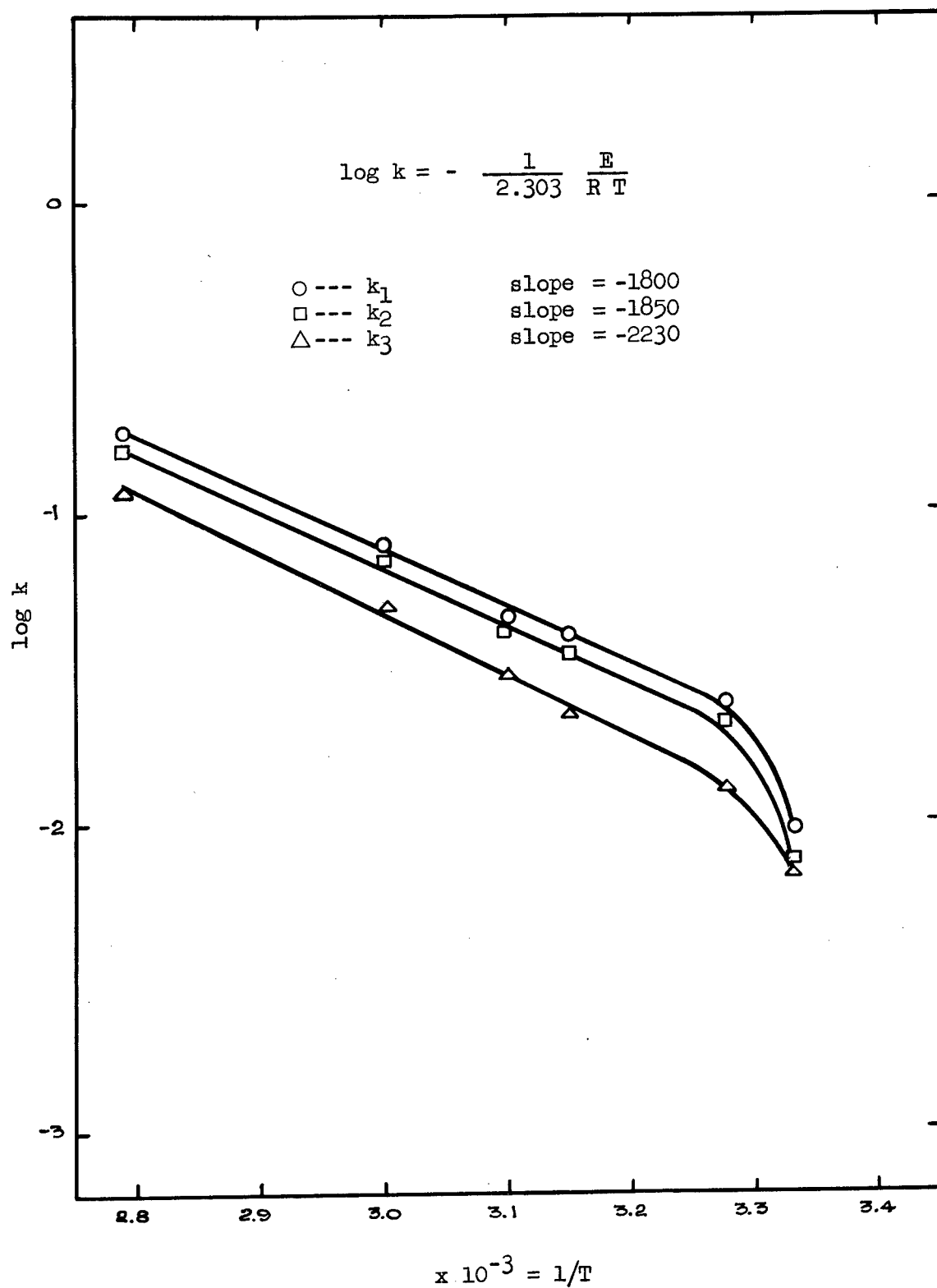


Fig. 8--Plot of $\log k$ versus $1/T$ for the data presented in Table VI.

DISCUSSION

It was stated earlier in this thesis that the reaction rates of uranium with H_2 , HD and D_2 might be expected to vary inversely as the square root of the reduced masses of the hydrogen molecules. Thus the ratio k_1/k_2 should be $2/\sqrt{3/2}$ or 1.15; k_1/k_3 should be $\sqrt{2}/1$ or 1.413 and k_2/k_3 $\sqrt{3/2}/1$ or 1.22. The data listed in Table V indicate good agreement at room temperature but relatively poor agreement for all other temperatures. However, from Figure 8 it is clear that the room temperature experiment did not fall in line with the other experiments when the Arrhenius equation was applied to the experimental data. Thus it becomes necessary to offer a plausible explanation for the general deviation of the experimental results from the principle mentioned above.

The experiments were designed to present as great a uranium surface as possible with which hydrogen molecules could come in contact. However, the use of finely powdered metal introduced an additional factor into the processes, that of adsorption. While the rates of reaction between uranium metal and hydrogen molecules might follow the inverse square root rule, the rates at which the different molecular species of hydrogen are initially adsorbed may constitute the over-all rate determining step in the processes. Complications due to adsorption may be sufficient to account for the observed variations from the inverse square root rule.

The over-all process is probably best considered as taking place in three steps: (1) The gas molecule approaches the metal surface and is adsorbed forming an adsorption complex. (2) The adsorption complex either has sufficient energy to become an activated adsorption complex or it lacks the requisite energy and breaks down, which is equivalent to stating that the gas molecules evaporate from the surface. (3) Those adsorption complexes which are activated are then converted to a compound. Thus only molecules which are adsorbed have an opportunity to react and only those which possess sufficient energy to form an activated adsorption complex take part in the reaction between gas and metal.

The uranium-hydrogen reactions must then be considered as taking place in a heterogeneous system and the activation energies observed are only apparent activation energies. If it is assumed that the product of the reaction does not have a retarding influence upon the rate of reaction, then

$$E = E_a + \lambda$$

where λ is the heat of adsorption of a mole of hydrogen by uranium and E is the true activation energy. The validity of this assumption is indicated by the fact that when hydrogen reacts with massive uranium the hydride formed continually sloughs off the metal surface allowing new surface to be exposed for reaction. A similar action is to be expected even in the case where finely powdered metal is employed since

the crystalline forms of hydride and metal are different. Even if the hydride should have some retarding influence upon the reaction rate, the fact that less than one-thousandth of the uranium metal would take part in compound formation if all the hydrogen used in any of the experiments was converted to hydride indicates that the extent of the retarding action would certainly be small and probably negligible. In order to determine the true activation energy for the reaction between uranium, H_2 , HD and D_2 it becomes necessary to know the heat of adsorption for these molecular species being adsorbed on uranium. Unfortunately, determination of the heats of adsorption is impossible since under none of the experimental conditions could the reaction between gas and metal be prohibited. An alternative is to consider other instances in which comparative studies on the heats of adsorption of H_2 and D_2 have been reported. Maxsted and Moon (10) determined the relative rates of adsorption of H_2 and D_2 from -21 to $50^\circ C$. on finely divided platinum and found the rate of adsorption of H_2 to be 1.4 to 1.5 times that of D_2 . They reported the energy of activation of the adsorption of the two gases to be 2500 calories mol^{-1} and 2400 calories mol^{-1} . Soller, Goldwasser and Beebe reported (11) that the relative rates of adsorption of D_2 and H_2 on finely divided copper and indicate H_2 to be adsorbed 5.5 times as rapidly as D_2 at 0° centigrade. A difference of 750 calories in the activation energies for the two kinds of hydrogen in the range of about 10,000 calories is indicated. Beebe and Dowden (12) reported the heats of adsorption for H_2 and D_2 on chromic oxide to be 4600 and 4950 calories respectively while values of 1000 and 1700 calories are listed for the adsorption on nickel (13) in the temperature range 0.25° centigrade. Maidanovskii and Bruns (14) indicated a value of 17,000 calories for the initial heat of adsorption of H_2 on platinum at 100 - $120^\circ C$.

The range over which the heats of adsorption of H_2 and D_2 are distributed on metals other than uranium makes it impossible to attempt any analogies in the estimation of a reasonable value for the true activation energy of the hydrogen-uranium reaction. Since it is not possible to actually measure the heats of adsorption of hydrogen on uranium the true activation energy for the reaction cannot be known. If the entire surface of uranium metal was covered with hydrogen molecules the amount adsorbed would not change with temperature and Δ would be zero, and E_a would be the true activation energy. However, this is unlikely under the conditions of the experiments and so the conclusion must be made that the true activation energies for the hydrogen-uranium reactions are less than the observed apparent activation energies but no actual values can be cited.

The report of Soller, Goldwasser and Beebe (11), in which it was indicated that the rate at which copper adsorbed H_2 was 5.5 times as rapid as the rate at which D_2 was adsorbed, indicates that the step in which hydrogen molecules are adsorbed on the uranium may be the controlling fact in the observed variations from the inverse square root rule.

The above discussion shows that the heterogeneous nature of the reaction system makes it difficult to accurately determine the relative rates of these processes.

An alternate viewpoint should be examined by which the phenomena observed in the experiments described in the third section of this thesis may be explained. If the rate of interaction between hydrogen and uranium does not depend upon the difference in zero point energies of the different molecular species it might involve diffusion of the molecules into the metal. Since the diffusion rates of gases depend inversely as the square root of their masses, the ratios of the reaction rate constants would be $k_1/k_3 = \sqrt{4}/\sqrt{2}$ or 1.415; $k_1/k_2 = \sqrt{3}/\sqrt{2}$ or 1.225 and $k_2/k_3 = \sqrt{4}/\sqrt{3}$ or 1.155. Comparison of these values with those cited in Table V gives as good agreement as the ratios based upon the zero point energies and no choice can be made between the alternate viewpoints. It is therefore necessary to consider other factors involved in the experiments before a choice can be made between the zero point energy and diffusion interpretations of the experimental data. McBain (15), in studies on the sorption of hydrogen by charcoal, observed that there was an initial rapid adsorption of the gas followed by a slower process. The rate of adsorption of the slow process was in agreement with the laws of diffusion. In the experiments described in this thesis the extremely short times during which observations were made necessarily exclude any diffusion into the metal. Brunauer (16) stated that it is generally safe to conclude that in a purely physical adsorption, gas molecules are adsorbed as rapidly as they reach the surface. The slow effects are due to chemisorption, chemical reaction, solution or to the inability of gas molecules to contact the surface of the metal.

Durau and Teckentrup (17) studied the purely physical adsorption of different gases, including hydrogen, on finely divided iron. They found that equilibrium was established very rapidly and the isotherms were completely reversible at 18° C. and for a pressure range 50-750 millimeter of mercury. Benton and White (18) observed the sorption of hydrogen by nickel and copper and Taylor and McKinney (19) studied the sorption of carbon monoxide by palladium; they found a very rapid initial stage which indicated purely physical adsorption followed by a slow stage in which the rate of sorption was very slow. This second stage was designated by Taylor (20) as activated adsorption.

Consideration of the observations made on the hydrogen-uranium reaction and the three steps by which the over-all process is assumed to proceed (see page 30 of this thesis) indicate that the first step is most likely purely physical adsorption and proceeds very rapidly. The second or activating step is the slow step while the third step is very rapid. Thus the over-all rate of interaction between uranium and hydrogen is controlled by the rate at which the activated complexes are formed. Since it has been shown in a previous discussion in this thesis that the rate of diffusion of the different hydrogen molecular species into the metal has little influence upon the rates at which reactions occur, the observed differences in the rates are probably due mainly to the difference in the zero point energies of the hydrogen molecules.

LITERATURE CITED

1. L. N. Ridenour and C. W. Lampson, Rev. Sci. Instr. 8, 162-164 (1937).
2. E. C. Marbae, Chem. Eng. News 27, 2198-2201 (1949).
3. A. O. Nier, M. G. Ingraham, G. Stevens and B. Rustad, A Mass Spectrometer for Routine Hydrogen Isotope Analyses, Declassified Manhattan Project Report MDDC-197, (Declassified July 26, 1946).
4. W. Bleakney, Phys. Rev. 41, 32-38 (1932).
5. H. Becquerel, Compt. rend. 122, 420-423 (1896).
6. B. B. Boltwood, Am. J. Sci. IV, 22, 537-538 (1906).
7. -----, Am. J. Sci. IV, 24, 370-372 (1907)
8. D. W. Wilson, A. O. Nier and S. P. Reimann, Preparation and Measurement of Isotopic Tracers, (J. W. Edwards Inc., 1946), p. 11.
9. J. J. Thompson, Rays of Positive Electricity and Their Application to Chemical Analyses (Longmans, Green and Co., 1913).
10. F. H. Spedding, A. S. Newton, J. C. Warf, O. Johnson, R. W. Nottorf, I. B. Johns and A. H. Daane, Nucleonics 4, 4-15 (1949).
11. S. Glasstone, Textbook of Physical Chemistry, (D. Van Nostrand and Co., 1940), p. 155.
12. B. A. Rogers and P. Chiotti, The Production of Uranium and Thorium in Powdered Form, ISC-31, Ames Laboratory of the Atomic Energy Commission, (Dec. 23, 1948).
13. E. B. Maxsted and C. H. Moon, J. Chem. Soc. 1936, 1542-1546 (1936).
14. T. Soller, S. Goldwasser and R. A. Beebe, J. Am. Chem. Soc. 58, 1703-1706 (1936).
15. J. W. McBain, Z. physik. Chem. 68, 471-497 (1909)
16. S. Brunauer, The Adsorption of Gases and Vapors, Vol. I, Physical Adsorption (Princeton University Press, 1942), p. 8.
17. F. Durau and C. H. Teckentrup, Ann. Physik 12, 297-935 (1932).
18. A. F. Benton and T. A. White, J. Am. Chem. Soc. 54, 1373-1390 (1932).
19. H. S. Taylor and P. V. McKinney, J. Am. Chem. Soc. 53, 3604-3624 (1931).
20. H. S. Taylor, J. Am. Chem. Soc. 53, 578-597 (1931).